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Synthesis and structure of ferrocenylphosphinic acids

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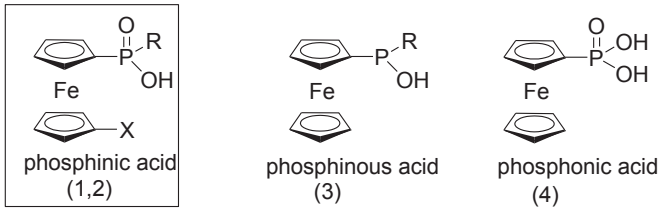
ABSTRACT

The series of ferrocenylphosphinic acids Fc(P(R)(O)(OH)) (**1a**–**d**) and ferrocene-1,1′-diyl-phosphinic acids Fc(P(R)(O)(OH))$_2$ (**2a**–**d**) (R = H (a), Me (b), Et (c), Ph (d)) have been obtained and studied using X-ray single crystal diffraction, IR-spectroscopy and quantum chemistry. The intermolecular hydrogen bonding in **1a**–**d** proceeds highly stereoselectively and results in formation of racemic conglomerate of **1d**. The formation of inter- and intra-molecular hydrogen bonds for disubstituted acids **2c**–**d** depends on substituent at phosphorus atoms.

Introduction

The arylphosphinic acids ArP(R)(O)(OH) (R = H, alkyl, aryl) are widely used for the construction of self-assembled two- and three-dimensional structures or single molecular magnets (SMM) based on p- [1], d- [2] and f- [3] metals, e.g., Ru [4] and Mn [5] complexes. The replacement of the aryl fragment in these acids for the cognate ferrocenyl fragment, containing redox-active iron atom, may result in additional interesting properties like enhanced exchange interactions and give the opportunity to make sensors or switchable devices.

However ferrocenylphosphinic acids (**1**,**2**) are poorly studied in contrast to other ferrocenyl-containing phosphorus acids. For example, ferrocenylphosphinous acids (**3**) existing as the mixtures of two tautomeric forms have been widely employed as ligands in transition metals catalysis of cross-coupling reactions [6,7], asymmetric hydrogenation [8] etc. Ferrocenylphosphonic acid (**4**) has been considered as redox-active pH-responsive molecule and the redox half-wave potential of ferrocenylphosphonates is sensitive to the bonding mode with metal atoms [9–14].



R = H: X = H (**1a**), P(O)(OH)H (**2a**)
R = Me: X = H (**1b**), P(O)(OH)Me (**2b**)
R = Et: X = H (**1c**), P(O)(OH)Et (**2c**)
R = Ph: X = H (**1d**), P(O)(OH)Ph (**2d**)

The data on the synthesis, structure and redox properties of ferrocenylphosphinic acids are scarcely presented, although their first synthesis dates back to 1962: Sollott and Howard found that ferrocene reacts with PCl_3 under Fridel–Crafts reaction conditions in the presence of $AlCl_3$ to form (**1a**) and (**2a**) with the yield of 3.2% and 4.6% respectively after the hydrolysis [15]. Diferrocenylphosphinic acid was also isolated from this mixture [16]. The yield of (**1a**) was slightly improved to 8.6% using Me_2NPCl_2 as starting reagent instead of PCl_3 [17]. The formation of (**1a**) as a side-product has been also observed in the hydrolysis of diphosphene

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